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16. Abstract Using, as an example, the study of the electrical conductivity of a number of ion exchange membranes as a function of the nature of the ionogenic groups, technology of manufacture (homogeneous, heterogeneous), and total exchange capacity, as well as the nature of the concentration and temperature of the solution, it is shown that the spatial distribution of ionogenic groups has a critical influence on the value of the electrical conductivity and not on their total number.			
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ELECTRICAL CONDUCTIVITY OF ION EXCHANGE MEMBRANES AND THE INHOMOGENEITY OF THEIR STRUCTURE

V. K. Varentsov and M. V. Pevnitskaya

The present paper deals with the influence of the inhomogeneity of the structure of ion exchange membranes on their electrical conductivity. Inhomogeneity of ionites has been discussed frequently in the literature [1]. Quantitatively, inhomogeneity of ion exchangers can be characterized by means of the mean-square deviation H_{ms} of the local values of the concentrations of the fixed ions from the average value I_0 [2]. /3*

Table 1 presents some of the physical-chemical characteristics of the membranes studied in this work. A detailed description of the methods used in the study will be found in [3]. As indicated by the data in the table, all of the membranes are inhomogeneous to a certain extent. In the case of heterogeneous membranes, H_{ms} is in the range from 50-99%, while for the so-called homogeneous ones the values of H_{ms} do not exceed 30% and mainly vary around 20%. At the same time, however, one can clearly see the correlation which exists between the values of the specific electrical resistance ρ and H_{ms} for membranes that have similar total exchange capacities.

The relationship between ρ and the exchange capacity has been studied in more detail in three series of samples of heterogeneous and homogeneous membranes. In preparing samples

*Numbers in the margin indicate pagination in the foreign text.

of each series, stress was placed upon the maintenance of a technological regime such that the membranes that were obtained differed from each other only in the concentration of ionogenic groups. The properties of the heterogeneous membranes are listed in Table 1. It is evident that the specific resistance of the cationite membrane decreases with their increasing content of KU-2* resin; when the amount of the latter is approximately 80% (by weight) ρ becomes quite close to a value characterizing the ion-exchange resin ($\rho = 29.2$ ohms/cm, $H_{ms} = 22.8\%$). The sharpest change in ρ is observed when the amount of ionite drops from 60 to 40%. The decrease in the amount of resin in the membrane from 80 to 40% is accompanied by an increase in the mean square deviation from 47 to 94%. If we examine the corresponding values of ρ and the Conductivity Exchange Capacity (CEC), it is clear that the exchange capacity then drops approximately by a factor of 1.9, while the electrical resistance increases much more sharply--by 8.6 times.

In the membranes of the MA-41 type, a sharper increase in the value of ρ is also observed (approximately by a factor of 4), while CEC decreases by a factor of 1.6. Similar relationships between ρ , CEC, and H_{ms} are observed when studying homogeneous membranes obtained by radiation grafting (Table 2). The different capacity of the membranes is related to the difference in the radiation doses of the materials. The development of a different degree of inhomogeneity of ion-exchange materials may be traced in the dependence of the permeability of the membranes upon the nature of the ionogenic group and the nature of the solution. Table 3 lists the values for ρ , H_{ms} , CEC and the exchange capacity by strongly basic and strongly acid groups for several ion exchange membranes, containing a certain percentage of weakly dissociating (under certain conditions) ionogenic groups.

* [Translator's note: expansion not known]

Membrane type	REC mg-eq g of dry mem- brane	Swel- ling in thickness in	area in	$\frac{1}{\rho} = \frac{0.01}{0.2}$ N. NaCl	ohm- cm 0.5N (NaCl)	K, $\frac{\text{cm}^3\text{-s}}{\text{g}}$	W, %	i_{pr} , mA/cm ² in 0.1N NaCl	H _{ms} , %	Thickness of membrane in H ⁺ form, mm
Homogeneous membranes										
FK-3	2,32	155	161	94,5	45,8	$5,4 \cdot 10^{-14}$	53	13,9	27,7	0,32
FK-26k	1,90	126	162	95,3	39,2	$3,3 \cdot 10^{-14}$	41	13,8	18,0	0,29
MPFS-26	1,90	120	140	97,5	91,5	$2,3 \cdot 10^{-14}$	34	13,2	21,9	0,21
FK	2,52	117	139	97,6	80,6	$2,2 \cdot 10^{-14}$	39	13,4	20,4	0,23
MK-100	2,50	131	153	99,0	120,0	$2,5 \cdot 10^{-14}$	32	13,3	21,8	0,17
MA-100	2,50	108	128	97,4	130,0	$9,5 \cdot 10^{-14}$	35,2	20,0	22,8	0,36
MVP-7	1,80	123	141	96,5	80,4	$3,6 \cdot 10^{-14}$	44,8	20,0	20,4	0,47
Heterogeneous membranes										
Content of pure grade KU-2-8 in MK-40 type membranes (%)	40 50 60 70 80	1,90 2,30 2,90 3,20 3,70	112/121 114/126 116/131 120/134 124/136	98,9 98,5 96,5 95,0 87,5	302,0 166,0 109,0 59,0 35,0	$5,4 \cdot 10^{-14}$ $9,9 \cdot 10^{-14}$ $5,1 \cdot 10^{-13}$ $3,2 \cdot 10^{-12}$ $1,8 \cdot 10^{-11}$	25 30 37 44 48	10,5 11,1 12,0 12,7 13,5	94,0 88,0 72,0 61,0 47,0	0,28 0,33 0,35 0,35 0,36
Content of anionite in MA-41 type membranes (%)	50 55 60 65	0,93 1,15 1,17 1,48	110/110 112/115 113/121 113/125	97,6 97,1 97,0 96,2	288,0 199,0 124,0 70,0	$2,3 \cdot 10^{-13}$ $1,1 \cdot 10^{-12}$ $2,5 \cdot 10^{-12}$ $1,2 \cdot 10^{-11}$	28 32 34 43	20,0 18,3 17,2 15,9	— — — —	0,62 0,65 0,67 0,61
MK-40	2,3	—	—	96,8	100,0	$2,1 \cdot 10^{-13}$	43	12,9	74,5	0,59
Membranes on KU-1 resin	3,2	—	—	91,0	196,0	$6,2 \cdot 10^{-10}$	45,0	13,1	—	0,48
MA-43	0,85	—	—	96,0	201,0	$7,8 \cdot 10^{-12}$	30,0	13,6	—	0,67
MA-40	3,2	—	—	86,1	128,6	$1,1 \cdot 10^{-13}$	43	19,3	83,2	0,58

These data were obtained in a 0.1 M solution of NaOH or HCl when all of the ionogenic groups were either in the Na⁺ or the H⁺ forms for cationites and in the Cl⁻ or OH⁻ forms for the ionites. In addition, the values given for ρ of the corresponding membranes in the solutions of NaCl were the same concentration. For comparison, Table 3 contains the characteristics of the monofunctional cationite and anionite membranes of the strongly acid and strongly basic types.

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Table 2

REC mg·eq grams of moist membrane	$\bar{\kappa}$ ohms ⁻¹ ·cm ⁻¹ in 0.5N NaCl	H _{ms} , %
2.5	3.1·10 ⁻²	36.0
2.0	2.0·10 ⁻³	67.6
1.2	5.0·10 ⁻⁵	74.0
0.5	1.2·10 ⁻⁵	98.8

TABLE 3

Type of membrane	CEC, mg·eq g of dry membr.	EC on strongly ionized groups	Ohm ⁻¹ ·cm ⁻¹ ·10 ⁻³ in 0.1 N solu- tions			H _{ms} , %	
			HCl	NaCl	NaOH	neutral medium	acid medium
MK-40	2.20	2.21	24.4	4.5	7.1	74.5	74.0
MK-41	3.90	2.1	16.8	8.3	10.9	59.0	84.5
Membrane c resin	3.20	1.8	6.1	4.2	5.8	—	—
KU-1	2.60	2.58	26.7	17.6	18.5	21.8	21.5
MK-100	0.85	0.79	2.5	2.0	9.4	99.5	97.1
MA-43	3.80	0.61	4.4	1.8	1.0	—	83.2
MA-40	1.66	0.97	9.8	8.8	3.4	30.8	14.3
MVP-7							

It follows from an examination of these data that all of the causes (formation of covalent bonds of H^+ with the mildly acid groups in the HCL solution or due to the hydrolysis in a NaCl solution; neutralization of mildly basic groups of anion-exchange membranes in alkaline solutions or due to processes of hydrolysis in solutions of neutral salts) lead to a simultaneous change in the amount of charge carriers in the membrane, the degree of inhomogeneity of the membranes and their electrical conductivity. All of the experimental data presented above indicate that there are the following relationships between the exchange capacity, degree of inhomogeneity and electrical conductivity of the ionite; (1) A decrease in the exchange capacity of anionite leads to an increase in its inhomogeneity and simultaneously to a drop in the electrical conductivity; (2) a drop in the conductivity takes place more sharply than the decrease in the capacity.

In this connection, it was concluded that the conductivity of the ionite is influenced not so much by the amount of fixed ionogenic groups as by their spatial distribution.

This becomes clear when we examine the mechanism for the transport of charges across the ion-exchange material. If we use a friable quasicrystal as a model of the ionite, the mixing of the charged particles in the ionite must be involved with the presence of defects in their structure [4, 5]. Consequently, the most probable mechanisms for the charged transport become the following:

- 1) Migration of anti-ions, located around the corresponding fixed groups, compensating their charge (normal position of the ion), to the "free" fixed groups which are adjacent at a given moment--vacancies (the so-called vacancy mechanism).

- 2) The movement of free anti-ions (penetrating ions) from one orbit to another.

3) So-called croquet mechanism, in which the penetrating ion extracts the adjacent ion from its normal position and takes its place, and the extracted ion moves to a new position, that of the penetrating ion. The ions of the Donnan /absorbed electrolytes constitute additional ions which have penetrated. In the ionites, obviously, all three mechanisms of charged transport occur simultaneously, except that the percentages of each of them can change as a function of the external conditions (temperature, concentration of the solution, percentage of binding in the ionite, and so forth). However in any case the probability of the jumping of a charged ion from one equilibrium position to another will increase as the positions of the ions in the ionite draw closer together and are more uniform throughout the entire volume--the anti-ions and especially the fixed ions. In other words, the electrical conductivity of the ionite is linked to the probability of the charged transfer, so that it is clear that the relationship of $\bar{\kappa}$ to the exchange capacity must be not linear but stepwise and that in a certain range of values $PoYe$ one can speak of the dominant influence of the degree of inhomogeneity of the ionite on its conductivity. /6

The experimental material obtained in this work shows that the nature of the inhomogeneity of the ionite is of no significance. In the case of heterogeneous membranes, the inhomogeneity lies in the specific nature of the technology of the preparation--the distribution of particles of ion-exchange resin in a mass of inert material. The conductivity of such a membrane is determined both

¹Thus far there has been a tendency to view the ionite as a material that possesses ionic conductivity.

by the shifting of charges within the ionite itself and on the films of solution which can form around the boundaries of the resin grains--an inert plastic. The change in the CEC as a result of the decrease in the content of ion exchange resin in the heterogeneous membrane decreases the possibility of the existence of continuous conduction parts along any channel: through the ionite alone, or through the solution alone, or through a mixture of the ionite and the solution. However the mechanism of transport with respect to the entire ionite or films of electrolyte is unaffected by the percentile change in the resin in the membranes course.

In homogeneous membranes, the reasons for inhomogeneity are different. First of all, there may be an isotropy of the physical-chemical properties of the original polymers; secondly, there may be inhomogeneity of the distribution of the fixed groups, caused by the statistical nature of the process of activation of the material; thirdly, when the dose of radiation is decreased there is a rise in the inhomogeneity of the penetration of the radiation into the mass of the future ionite. In other words, a decrease in the exchange capacity in homogeneous membranes influences the mechanism of permeability of the ionite itself--it changes the ratio of the above-mentioned mechanisms with respect to vacancies, with respect to the penetration of ions and the croquet mechanism.

According to the data in Table 3, as the number of ionogenic groups decreases, regardless of the nature of the original inhomogeneity, there is a still greater decrease in the probability of the discontinuous movement of the ions in the ionite, i.e., there is a sharp increase in the electrical resistance of the ion exchange material. Heterogeneous membranes of methyl-red 40 and

MA-43 are practically monofunctional, and the ionogenic groups belong to the "strong electrolyte types"--the SO_3H and $-\text{N}(\text{CH}_3)_3$ groups. The electrical conductivity of these membranes in solutions of HCl , NaOH and NaCl changes only in accordance with the changes in the mobility of the anti-ions $\text{H}^+ \rightarrow \text{Na}^+$, $\text{OH}^- \rightarrow \text{Cl}^-$. However, in the case of the MA-40 and MVP-7 membranes, the relationship of the electrical conductivity on the degree of neutralization of the slightly dissociating groups has been clearly demonstrated and the mobility of the anti-ions does not play an important role. The MVP-7 membrane ($H_{\text{ms}} = 14.3\%$) contains 43.4% of the mildly basic groups. When they are completely neutralized (exchange capacity drops by 1.7 times) and there is a simultaneous replacement of the Cl^- anti-ion by a more mobile OH^- ion, the electrical conductivity of the membrane drops from $9.8 \cdot 10^{-3}$ to $3.4 \cdot 10^{-3} \text{ ohms}^{-1} \cdot \text{cm}^{-1}$, i.e., by a factor of 2.8. 17

Hydrolysis of the mildly basic groups in the NaCl solution also has a much stronger influence on the conductivities of the MA-40 membranes:

$$\frac{\kappa_{\text{HCl}}}{\kappa_{\text{NaCl}}} = 2.4;$$

for MVP-7 its ratio is 1.1.

The decrease in the probability of the movement of charges during increasing inhomogeneity of the material is indicated by data obtained from the temperature relationships of the electrical conductivity of various ionite membranes. Table 4 presents the values of the electrical conductivity of certain membranes in various types of solutions as well as the values of the so-called energy of activation of electrical conductivity and the entropic terms indicating "excitations", taking place in the surrounding medium with a transfer of the anti-ion into the activated state [6]. The energies of activation are calculated from the

Table 4

Type of Membrane	Nature of the 0.1N solution	$\bar{\kappa}, \text{ohm}^{-1} \cdot \text{cm}^{-1} \cdot 10^{-3}$	$\bar{D} \cdot 10^{-7}, \text{cm}^2 \cdot \text{sec}^{-1}$	$\lambda \left(\frac{-\Delta s}{R} \right) \cdot 10^{-8}$	$E_{\text{act}}, \text{kcal/mole}$
MK-40	HCl	24.4	46.1	0.7	2.6
	NaCl	4.5	8.6	0.5	3.2
	NaOH	7.1	13.5	0.6	3.2
Membrane on resin KU-1	HCl	6.1	22.6	16.7	8.55
	NaCl	4.8	6.7	1.2	4.1
	NaOH	5.8	8.0	1.8	4.4
MA-43	HCl	2.5	8.4	1.4	4.2
	NaCl	2.8	6.3	0.3	3.0
	NaOH	9.4	31.4	0.7	2.8
MA-40	HCl	4.4	5.5	0.7	3.7
	NaCl	1.8	2.2	3.6	4.6
	NaOH	1.0	7.6	32.2	7.4

temperature relationships of the electrical conductivities using the relationship

$$\bar{\kappa} = A e^{\frac{E_{\text{act}}}{RT}} \quad (1)$$

Calculation of the entropic terms was calculated on the basis of data obtained from electrical conductivity on the temperature relationship of the coefficients of diffusion in corresponding membranes. To calculate \bar{D} , we use the relationship

$$\bar{D} = \frac{RT\bar{\kappa} \cdot 1000 \cdot \bar{t}}{zT^2 \cdot E} \quad (2)$$

(E is the total exchange capacity of the ionite); to calculate the entropic term

$$\bar{D} = c \lambda^2 \frac{kT}{h} e^{-\frac{\Delta S}{R}} e^{-\frac{E_{act}}{RT}}, \quad (3)$$

where λ is the distance between two adjacent positions of equilibrium for the movement of an ion; k is Boltzman's constant; h is Planck's constant; T is the temperature in °K and ΔS the increase in entropy. In the case of completely dissociated iogenic groups such as E_{act} and $\lambda \left(e^{-\frac{\Delta S}{R}} \right)^{1/2}$ do not differ from from 2-4 and 1 kcal/mole, respectively. These values are close to the corresponding values of the activation energy and the entropic term, characterizing the diffusion of ions, determining the conductivity of membranes, in a solution with a lack of specific interactions with the medium. However, if the ionite contains neutralized slightly-dissociating groups, E_{act} will increase to 8-12 kcal/mole and the entropic term will increase sharply. This is clearly produced both by the predominance of the forces of the specific interaction with the ionogenic groups and the increasing steric obstacles which arise when the ions move in the ionite.

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